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भाग 4 जल में घुली आक्सीजन का मापन

Indian Standard

EXPRESSION OF PERFORMANCE OF ELECTROCHEMICAL ANALYZERS

PART 4 STANDARD FOR MEASURING OXYGEN DISSOLVED IN WATER

ICS 71.040.40, 13.06.20

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Electronic Measuring Instruments, Systems and Accessories Sectional Committee, LTD 21

FOREWORD

This Indian Standard (Part 4) was adopted by the Bureau of Indian Standards, after the draft finalized by the Electronic Measuring Instruments, Systems and Accessories Sectional Committee had been approved by the Electronics and Telecommunication Division Council.

The objective of this standard is to specify the terminology, definitions, requirements for statements from manufacturers and performance tests for sensor units, analyzers, and electronic units used in the determination of the dissolved oxygen contents of aqueous solutions.

Annex A of this standard provides general information on amperometric oxygen sensors used for measuring dissolved oxygen in water.

While preparing this standard (Part 4) assistance has been derived from IEC Pub 746 (Part 4) : 1992 'Expression of performance of electrochemical analyzers, Part 4 Dissolved oxygen in water measured by membrane covered amperometric sensors' issued by the International Electrotechnical Commission (IEC).

This standard (Part 4) is one of the parts of IS 13673 series of standards on performance of electrochemical analyzers. The other parts of the series are:

Part 1 General,
Part 2 *p*H value,
Part 3 Electrolytic conductivity, and
Part 5 Oxidation-reduction potential or redox potential.

In reporting the results of a test or analysis made in accordance with this standard, if the final value observed or calculated, is to be rounded off, it should be done in accordance with IS 2 : 1960 'Rules for rounding off numerical values (*revised*)'.

Indian Standard

EXPRESSION OF PERFORMANCE OF ELECTROCHEMICAL ANALYZERS

PART 4 STANDARD FOR MEASURING OXYGEN DISSOLVED IN WATER

1 SCOPE

1.1 This standard applies to analyzers using membrane covered amperometric sensors for the continuous determination of dissolved oxygen partial pressure or concentration. It applies to analyzers for use on potable water, industrial process streams, industrial waste water, municipal waste water, and receiving bodies of water (for example lakes, rivers and estuaries). Though not specifically applying to non-membrane covered electrochemical sensors, the discussion of analyzers utilizing membrane covered amperometric sensors may be used as a general reference.

2 REFERENCE

2.1 The Indian Standard listed below is a necessary adjunct to this standard:

IS No.	*Title*
IS 13673 (Part 1): 1993	Expression of performance of electrochemical analyzers : Part 1 General

3 DEFINITIONS

The definitions contained in IS 13673 (Part 1) and the following apply for the purpose of this standard.

3.1 Symbols

pO_2 = partial pressure of oxygen in the gas phase during equilibrium conditions with the solution, and

cO_2 = concentration of dissolved oxygen in a solution.

3.2 Membrane Covered Amperometric Sensor Unit

A sensor unit usually consists of a cathode, where electrochemical reduction of molecular oxygen occurs (typically fabricated from gold, silver, or platinum), an anode (typically silver or lead) where a well defined, electrochemically reversible oxidation reaction occurs, an appropriate electrolyte and an appropriate polymeric diffusion limiting membrane separating the sensor from the test medium. Another function of the membrane is to isolate the sensor electrodes and electrolyte from the many forms of contamination which are generally present in aqueous samples. Membrane covered amperometric oxygen sensors can function either as a voltage driven electrochemical cell or as a galvanic cell.

3.3 Influence Quantities

3.3.1 *Temperature*

Temperature affects the performance of membrane covered amperometric dissolved oxygen sensors by changing the oxygen permeability of the diffusion limiting membrane. This is a reversible process. When sample temperature changes occur, the solubility of oxygen dissolved in the sample will change, so for instruments reading out directly in concentration, some compensation for the variation of oxygen solubility with temperature is usually conducted.

The change in the output signal of a sensor unit caused by variations in sample temperature depends on two factors: (1) increased membrane permeability caused by temperature increase, and (2) changes of the oxygen solubility in water with temperature; the second factor works only when the instrument is calibrated in concentration units (ppm. mg/l). Sensitivity is a ratio of the sensor unit output to the sample saturation degree (%), partial pressure of concentration, according to the accepted calibration.

3.3.2 *Pressure*

Pressure effects are important when the dissolved oxygen sensor is calibrated in the gas phase, since membrane covered amperometric oxygen sensors measure the partial pressure of oxygen, pO_2, which is directly proportional to the absolute pressure, when in a gaseous sample. Care must be taken during air calibration procedures to account for the atmospheric barometric pressure and to correct for the partial pressure of water which may be present in the calibration sample.

Sample pressure variations may cause rupture of the diffusion limiting membrane if the pressure specification of the sensor is exceeded. Some sensors are available which pneumatically transmit the stream pressure to the backside of the membrane to eliminate or minimize the pressure differential across the membrane.

3.3.3 *Dissolved Solids*

Dissolved solids present in an aqueous sample reduce the solubility of oxygen from that found in pure water. Tables for oxygen solubility in water containing dissolved solids should be consulted as a reference when analysis is conducted on other than pure water samples. This is important if the analyzer is calibrated in concentrations units.

3.4 Units

The amount of oxygen dissolved in water may be expressed in several ways and units.

3.4.1 Units for expressing the partial pressure of oxygen, pO_2, are either the millibar or the pascal.

3.4.2 Percent (%) is the unit used to express the actual oxygen concentration as a percentage of the solubility of atmospheric oxygen in equilibrium with water at the actual barometric pressure and the actual temperature, salinity and vapour pressure of the water.

3.4.3 The units for the expression of dissolved oxygen concentration, cO_2, as a ratio of the mass of dissolved oxygen to the mass of water are:

parts per million (ppm) ——— mg kg^{-1}
parts per billion (ppb) ——— $\mu\text{g kg}^{-1}$

NOTE — For most practical applications the density of water is so close to 1 000 (kg m^{-3}) that mg l^{-1} and ppm are used interchangeably. When the density of the sample deviates significantly from one, appropriate corrections should be made.

3.4.4 The units for the expression of temperature sensitivity are µA/mg/°C.

3.4.5 The units for the expression of oxygen consumption are milligrams per hour per ppm for dissolved oxygen sensors and in milligrams per hour per percent O_2 for gaseous oxygen sensors.

3.5 Zero Drift

The shift in reading for zero calibration mixture, over a stated period of time.

3.6 Span Drift

The shift in span over a stated period of time.

3.7 Polarization Voltage

The voltage applied to an amperometric cell which is driven with an external power supply. It is selected such that a linear relationship exists between the sensor current and the oxygen concentration.

3.8 Sensitivity

The change in electrode current caused by a unit change in oxygen concentration.

4 PROCEDURE FOR STATEMENT

See IS 13673 (Part 1) and the following:

> The manufacturer shall provide statements on the sensor unit and the electronic unit as indicated in 4.1 and 4.2.

4.1 Zero and Span Drifts

See IS 13673 (Part 1) and the following:

> Zero and span drift must be stated and are used as a substitute for the statement of stability.

4.2 Additional Statements on Sensor Units

4.2.1 Composition of electrodes contained within the sensor.

4.2.2 Internal filling solution.

4.2.3 Polarizing voltage.

4.2.4 Type of membrane material employed with sensor.

4.2.5 Residual signal [the output of the sensor when exposed to a gas with a certified low oxygen content (for example 1 ppm) and no cross interfering species or to a zero calibration solution].

4.2.6 Oxygen consumption by a sensor unit should be expressed in milligrams of oxygen per hour per litre of solution at a specified temperature and dissolved oxygen concentration.

4.2.7 Sensitivity.

4.2.8 Temperature dependency.

4.2.9 Type of temperature sensing equipment incorporated in sensor.

4.2.10 Stabilization time. If no time is stated, the manufacturer should be consulted.

4.2.11 Sample flow rate requirements.

4.2.12 Sensor pressure compensation technique, if relevant.

4.2.13 Whether sensor can be refurbished. Method and extent.

4.2.14 Dimensions of the sensor and a statement of materials of construction in contact with the solution.

5 RECOMMENDED STANDARD VALUES AND RANGES OF INFLUENCE QUANTITIES AFFECTING THE PERFORMANCE OF ELECTRONIC UNITS

See 5 of IS 13673 (Part 1).

6 VERIFICATION OF VALUES

See 6 of IS 13673 (Part 1) and the following.

NOTE — During all tests, appropriate corrections shall be made for changes in sample pressure. Testing done in this clause shall be conducted with the sample temperature within ± 0.2°C of the reference temperature, unless otherwise stated.

6.1 Calibration Solutions

See Annex B and Annex C.

6.2 Simulator for Testing Electronic Units

6.2.1 Testing of electronic units for linearity may be accomplished by the use of a suitable current source to substitute for the sensor. Caution should be used to make sure that temperature compensation devices or substitutes are still part of the electronics so that the unit is fully operable and that with electronic units employing a polarization voltage source for the sensor no interaction occurs between the voltage source and the sensor simulating current source. Alternatively, for electronics units employing a polarization voltage source for the sensor, fixed value resistors may be substituted for the sensor to simulate the sensor output current (the same precaution about use of temperature compensation elements is applicable).

6.2.2 Testing procedures for electronic units for adequacy of compensation changes in membrane permeability with temperature, and compensation for changes in oxygen solubility with temperature are highly dependent on the specifics of the individual electronic instrument design and thus no general test procedures may be currently designated.

6.3 Test Procedures for Sensor Units and Analyzer

6.3.1 *Operating Error*

A signal representing approximately the mid-scale value of the rated input range, resulting from the exposure of the sensor unit to an appropriate level dissolved oxygen, is used to test for operating error as described in **6.7.1** of IS 13673 (Part 1), whether testing an analyzer or a sensor unit.

6.3.2 *Linearity Error*

6.3.2.1 *Sensor units*

Using an appropriate electronic unit, perform the test as described in **6.3.2.2**.

6.3.2.2 *Analyzer*

The sensor unit is exposed to calibration solutions of known dissolved oxygen content representing nearly zero, nearly full scale and at least three intermediate calibration points whose values are approximately uniformly distributed. It is important to provide adequate stirring. The analyzer's final output readings are recorded. These steps are repeated once and the linear least-squares curve fit is calculated using both readings for each calibration point. The linearity error is determined graphically or numerically and expressed in terms of percent or rated range and is the maximum deviation for the least squares fit line.

NOTE — For reasons of efficiency this test can be combined with the test for repeatability (*see* **6.3.3.2**).

WARNING — Care must be taken when working with open containers due to the effects of air or gas humidity. Oxygen diffusion from outside can change the dissolved oxygen level in the test solution.

6.3.3 *Repeatability*

6.3.3.1 *Sensor unit*

Using an appropriate electronic unit, perform the test as described in **6.3.3.2**.

6.3.3.2 *Analyzer*

The sensor unit is exposed to test solutions representing as nearly as possible the minimum, the maximum and the median rated values. The steps are repeated N times (where $N > 6$) in each test solution in turn, at intervals of at least ten times the instruments 90 percent time. The recorded readings are converted to concentration units. The standard deviation is calculated for each set of recorded values for each solution and reported as repeatability.

6.3.4 *Interference Error for the Analyzer*

Since dissolved oxygen concentration depends on temperature, pressure and salinity, changes in these variables will cause a deviation of the output of the sensor from the relationship established under calibration conditions. This deviation is equivalent to an interference error. Due to the complex nature of the inter-relationships, the method of testing of this error is left for agreement between the manufacturer and the user.

6.3.5 *Zero Drift and Span Drift*

6.3.5.1 *Sensor unit*

Using an appropriate electronic unit, perform the test as described in **6.3.5.2**.

6.3.5.2 *Analyzer*

The sensor is exposed for 20 times T_{90} to a near-zero calibration solution or test solution. The recorder reading is adjusted to approximately 5 percent of full scale and recorded as a 'live zero'. The sensor is then exposed for 20 times T_{90} to a calibration solution or a test solution that gives a reading between 75 percent and 95 percent of full scale. The difference between the two readings is noted. The test is repeated without further adjustment after the specified time interval [*see* **6.7.4** of IS 13673 (Part 1)] which is used for stability determinations.

The zero and span drift errors are reported in terms of percent of the rated range.

6.3.6 *Output Fluctuation for the Analyzer*

The senor is exposed for 20 times T_{90} to a near-zero calibration solution or stable test solution. The recorder reading is adjusted to approximately 5 percent of full scale to serve as a "live zero" and the output is recorded for 5 min. The maximum peak to peak value of the deviations is determined in terms of percent of the rated range.

The test is repeated three times and the average of the readings is reported.

NOTE—For the purpose of this standard, spikes caused by the influence of external electromagnetic fields or by mains supply spikes are considered as being due to changes in influence quantities and are therefore ignored in the determination of output fluctuation.

6.3.7 *Delay Time (T_{10}), Rise Time (T_r), Fall Time (T_f) and 90 percent Time (T_{90})*

6.3.7.1 *Sensor unit*

Using an appropriate electronic unit, perform the test as described in **6.3.7.2** or **6.3.7.3** depending on the sensor type.

6.3.7.2 *Analyzers incorporating flow cells*

Two calibration solutions or stable test solutions must be provided with means of supplying either to the analyzer inlet, at rated flow, selected by appropriate means at the inlet port. The two test solutions shall differ in dissolved oxygen concentration by at least 50 percent of the rated range.

With a recorder connected to its output terminal, the analyzer is flushed with near-zero test solution until a constant reading is obtained. Then the upscale test solution is introduced and a mark is made on the recorder chart. Flow is continued until a constant reading is obtained. The values for delay time, rise time and fall time are determined from the chart. Flow is continued until a constant reading is obtained.

The value for 90 percent time is obtained by addition of the delay time and the rise or fall time, whichever is the larger.

6.3.7.3 *Analyzers incorporating immersion-type sensors*

The test is similar but the two test solutions are held in open containers of at least 10 litre capacity, and provided with appropriate stirring. The sensor is transferred from one container to the other and marks are made on the recorder chart at the moment of immersion. Care should be taken to compensate for air humidity effect and for possible intrusion of ambient air.

WARNING — Care should be taken to prevent exchange of the ambient air with test solutions.

6.3.8 *Temperature Effects*

The complete test is performed twice with the temperature of the test solutions at a minimum of two different test temperatures depending on the application of the instrument. The actual test temperatures shall be reported. A suitable test method is described in Annex B. This method determines the overall bulk temperature effect.

6.3.8.1 The capability of the sensor electronic unit to compensate for changes in membrane permeability due to temperature changes is an important parameter. This shall be functionally tested on a test solution of known concentration with perfect temperature compensation. Variation of the sample temperature over a realistic range, such as 0 to 50°C, should cause no change in the analyzer output. Deviations from ideal behaviour may be noted and used as a measure of the inadequacy of the temperature compensation.

6.3.8.2 The capability of the sensor electronic unit to compensate for the changes in solubility of oxygen in water with changes in temperature is an important parameter. This shall be tested by exposing the sensor to air saturated test solutions at various temperatures over the range of interest, for example 0 to 50°C, and doing a simultaneous wet chemical determination on the test solution to note the agreement of the instrumentally determined and wet chemical test determined dissolved oxygen concentrations. Because the sensor is an oxygen partial pressure sensor and the solution is saturated at all test temperatures, a partial pressure output from the sensor will indicate a constant value; in some cases, this is corrected by a temperature measurement which allows electronic computation of a correction factor to be automatically applied to the partial pressure signal to modify it to the correct dissolved oxygen concentration.

6.3.8.3 *Range and accuracy of temperature compensation*

Isothermal tests of the response of the instrument do not allow assessment of the time constant of circuits of automatic temperature correction, which can influence the magnitude of the reading.

Additional tests on the response of the instrument with changes of temperature are required, for example:

First Solution	*Second Solution*
+10°C, zero saturation	+30°C, 100% saturation
+30°C, zero saturation	+10°C, 100% saturation

In the case of flow type analyzers the temperatures of the sample loop may be changed by circulating it through a laboratory heating/cooling bath.

6.3.9 *Operating Period for Analyzer*

The test for operating period is the most comprehensive test included for the verification of values stated by the manufacturer for the performance of the analyzer. It represents the combination of conditions which constitute the worst case and therefore substitutes for complete verification of operating error.

Three important influence quantity effects which are not tested here are those of interfering components, sample temperature and sample pressure. Interference is not tested since it depends on components and concentrations agreed upon by the manufacturer and the user for each specific application (*see* **6.3.4**). Sample temperature and pressure effects are stated and tested separately. Standard temperature and pressure conditions during testing are assumed.

6.3.9.1 This test is performed under reference conditions except as otherwise stated..

After the start of the test, the analyzer shall not be adjusted by external means.

The analyzer is calibrated according to the manufacturer's instructions immediately before starting the test and it is operated according to the manufacturer's instructions during the test.

6.3.9.2 The sensor unit is exposed to a calibration solution that gives a reading between 75 percent and 95 percent of rated range and the reading is noted.

The analyzer is operated for at least the stated operating period and readings on the test solution are obtained at intervals of at the most, one-fifth of the operation period if it is one hour or less, or intervals of, at the most, one-tenth of the stated operating period if it is three hours or more.

All readings taken within the stated operating period must agree with the conventionally true value of the test solution, within the stated operating error.

6.3.9.3 Conditions under which the test is performed are reference conditions except as follows.

The supply voltage shall be at the minimum value of the stated limit range of operation when at least one reading is taken on the test solution and at the maximum value when at least one other reading is taken on the test solution. Likewise, the supply frequency shall be at the minimum value of the stated limit range of operation for one reading and at the maximum value for another. The deviations in voltage and frequency from their reference values need not be simultaneous.

If the operating period is three hours or more, the ambient temperature shall be at the minimum value of the stated limit range of operation when one reading is taken and at the maximum value of the stated limit of operation when another reading is taken. The deviation of ambient temperature from its reference value need not be simultaneous with the deviation of voltage or frequency from their reference values.

The rate of change of ambient temperature should not exceed the limits of rates of change stated by the manufacturer.

If necessary, in order to complete the tests involving changes in the operating conditions, according to the above procedure, a second, or third operating period test will be performed in order to include all of them.

6.3.10 *Determination of Sensor Unit Residual Signal*

The sensor unit is exposed to a calibration solution representing zero oxygen concentration containing no cross interferences. These solutions may be conveniently prepared by saturating a demineralized water solution with pure nitrogen passed through a fine porosity fritted bubbler. Alternatively, one may use a 2 percent sodium sulphite solution in demineralized water. Precautions should be taken to eliminate the possibility of back diffusion of atmospheric oxygen. The magnitude of the analyzer output signal after 20 times the T_{90} time is reported as the residual signal.

6.3.11 *Oxygen Consumption*

The sensor unit is exposed to a representative oxygen source (gaseous or dissolved) and the output current is measured. The oxygen consumption is computed from the following relationship.

$$\text{mg h}^{-1}\ O_2 = 2.97 \times 10^{-4}, (\mu\text{A Sensor Current})$$

By knowing the conversion factor between µA sensor current and percent gaseous oxygen or ppm dissolved oxygen, one may express this oxygen consumption data in the appropriate units.

ANNEX A

(*Foreword*)

SUPPLEMENTARY GENERAL INFORMATION ON AMPEROMETRIC OXYGEN SENSORS

A-1 Performance characteristics of the sensor are established by its electrochemical and mass transport characteristics. When utilizing an amperometric sensor with an external polarization voltage source, an electrical potential is impressed across the electrodes; in galvanically operating sensors, no external polarizing voltage source is required. In operation, the current due to the oxygen present in the test sample is determined solely by mass transport through the membrane/electrolyte interfaces, not by electrochemical kinetic limitations with equilibrium oxygen sensors. Operating in this mode the sensor displays an output current that is proportional to oxygen content, over the range of essentially zero oxygen concentration to full saturation in the liquid phase (and from 0.00 to 100 percent O_2 in the gas phase).

The dissolved molecular oxygen present in aqueous solution is in equilibrium with molecular oxygen dissolved in the sensor membrane and electrolyte. The flux of molecular oxygen determines the output current of the sensor and is determined by the activity of the oxygen dissolved in solution which is proportional to the dissolved oxygen concentration. In practical situations, due to the proportionality of activity and concentration and to the non-equilibrium state of most samples, it is preferable to relate the sensor output current to the dissolved oxygen concentration.

The oxygen reduction reaction is most generally conducted on a noble metal electrode (Au, Pt or Rh). Silver has also been used as a working electrode but is susceptible to poisoning by H_2S and other sulphur compounds. The overall reduction mechanism for oxygen at the cathode may be expressed as:

acid solutions $O_2 + 4H^+ + 4e^{-1}$ .... $2H_2O$;
alkaline solutions $O_2 + 2H_2O + 4e^{-1}$ .... $4OH^-$

The corresponding reaction at the anode is dependent on the choice of anode material and electrolyte. The most widely used anode material for voltage driven amperometric sensors is silver which reacts as follows:

chloride containing solutions
$Ag + Cl^-$ .... $AgCl + e^-$
alkaline solutions
$2Ag + 2OH^-$ .... $Ag_2O + H_2O + 2e^-$

For galvanic amperometric sensors the most commonly used anode materials are Cd or Pb, which are oxidized in alkaline electrolytes as follows:

$Cd + 2OH^-$ .... $Cd(OH)_2 + 2e^-$
$Pb + 2OH^-$ .... $PbO + H_2O + 2e^-$

For equilibrium sensors oxygen is produced at the anode as follows:

$4\,OH^-$ .... $O_2 + 2H_2O + 4e^-$

Several factors other than oxygen concentration related parameters affect the output signal generated by the oxygen sensor. Changes in pressure of the sample affect the partial pressure of oxygen present in the sample of dissolved oxygen in water. Pressure affects the solubility of the dissolved oxygen. Changes in the ionic strength of the test sample influence the dissolved oxygen activity. Changes in the temperature of the test sample not only affect the solubility of the dissolved oxygen present in the test sample, but can greatly influence the rate of oxygen diffusion through the diffusion limiting polymeric membrane incorporated in the sensor.

Temperature compensation of membrane permeability is usually conducted automatically in most instruments by measuring the temperature of the test sample and correcting the output signal of the sensor by the electronic means to make it invariant with changes in sample temperature. This is sometimes not done automatically, but by manual adjustment. Most modern analyzers incorporate not only means for correction of the membrane permeability with temperature but also for the variation of oxygen solubility with temperature so that a correct electronic conversion from the oxygen partial pressure measurement to a mg l^{-1} measurement is correct.

A-2 PRECAUTIONS

The use of plastic tubing should be minimized as diffusional partial pressure leaks may occur across the tubing walls. Diffusional leaks may also occur in fitting connections which appear to be correctly made up when tested with conventional leak testing equipment.

The sensor should be periodically calibrated to check its zero and span values to ascertain correct function and to eliminate the possibility of false oxygen readings due to sensor poisoning or internal failure.

Since the oxygen sensor consumes oxygen in the measurement process, it is required that adequate flow past the face of the sensor be provided to supply fresh, representative sample, undepleted in dissolved oxygen, to the sensor face for analysis. Sensors utilizing small cathodes or operating on a pulsed, discontinuous basis, suffer less from this limitation.

Contamination of the sensor membrane can result in reduced sensitivity and an increase in the response time of the sensor to oxygen concentration changes. Contamination may be inorganic as in the case of coating with ion hydroxides or organic as with oils or gases.

Though the diffusion limiting membrane of the sensor is ionically impermeable, dissolved gases such as H_2S, HCN and organic materials can dissolve in the membrane material and diffuse into the sensor with resultant contamination of the electrode materials of the sensor or the sensor electrolyte.

ANNEX B

(*Clauses* 6.1 *and* 6.3.8)

TECHNIQUE FOR THE PREPARATION OF BATCH CALIBRATION STANDARDS BY THE SATURATION APPROACH

B-1 Basically, 'standard' oxygen solutions are created by saturating an entire test bath with oxygen-nitrogen gas mixtures. If the temperature and salinity of the bath are known, then the dissolved oxygen content at saturation can be determined. When air (20.95 percent O_2 in N_2) is used as the saturation gas, dissolved oxygen values in fresh water which vary from about 6.9 to 14.4 ppm and in salt water from 4.7 to 11.3 ppm for temperature from 0°C to 35°C can be produced. Different dissolved oxygen ranges can be observed by using oxygen-nitrogen mixtures of other compositions. For instance, if a gas mixture of 20.95 percent per 2 percent O_2 in N_2 were used, the dissolved oxygen range would be from 3.5 to 7.2 ppm in fresh water since, by Henry's Law, the amount of oxygen that dissolves is directly proportional to the partial pressure of oxygen in the saturating gas mixture.

First, the instruments are calibrated at 20°C by placing them in a bath saturated with air (20.95 percent O_2) and making the necessary adjustments to their controls so that their outputs indicate the value for air saturated salt water at 20°C. Then the test bath is temperature cycled and resaturated at each test temperature, that is, bath temperature is changed to 10°C, 0°C, 10°C, 20°C, 30°C, 40°C, 30°C, 20°C, resaturated at each test point and instrument readings recorded at each temperature. The cycling procedure is repeated for a total of three cycles with each of five gas mixtures. In each case, the instruments are calibrated at 20°C in the 20.95 percent O_2 saturated bath before each cycle is run. A typical cycle requires approximately ten hours to run so that calibration is not reset during that time.

The technique used to saturate test baths is fairly simple. The saturation gas is passed through a stone aerator on the bottom of a temperature controlled bath that is well mixed. Various tanks with capacities ranging from 10 to 150 gallons are used. The first step in the procedure when using a new test set-up is to determine the amount of time required to saturate the bath. This is accomplished by placing any functional dissolved oxygen instrument sensor in the bath and lowering the bath temperature to 2°C. When the bath reaches temperature, air is started bubbling and dissolved oxygen content is read from the instrument at 5 to 10 minutes intervals. Eventually the dissolved oxygen value levels out. This, plus about 5 additional minutes, is taken to be the maximum saturation time for the bath and it is used as the bubbling time to saturate the bath at each test temperature. At each test point, the saturating gas is bubbled through the bath for the required time, aeration is stopped and sufficient time is allowed for bubbles to reach the water surface and disperse; the sensors in the bath are shaken to dislodge any bubbles on the membrane surfaces and readings are recorded.

ANNEX C

(*Clause* 6.1)

CALIBRATION SOLUTIONS FOR LOW LEVELS OF OXYGEN IN WATER MEASUREMENT

C-1 This system is used to:

a) reduce the oxygen concentration of air equilibrated water to a stable level of 1.0 ± 0.25 $\mu gO_2/l$.

b) enable the resulting liquid from (a) to be adjusted to any level within the range 1.0 to 50.0 $\mu gO_2/l$ in a time period of approximately 15 minutes. This is accomplished by adding to the main high purity nitrogen gas flow (1.0-1.5 l/min) a secondary flow (100-200 ml/min) of 0.1 percent or 0.5 percent oxygen in nitrogen. Adjustment of the relative flow rates allows the dissolved oxygen concentration to be set at will.

c) enable the calibration solution resulting from (b) to be held within ±1.0 $\mu gO_2/l$ over a minimum period of twelve hours.

d) deliver up to 800 ml/min of calibration solution continuously at a pressure of 0.5 bar.

C-2 DESCRIPTION AND OPERATION OF THE SYSTEM

The complete apparatus is shown schematically in Fig. 1 and consists of a steam stripping rig unit (Block A) connected by a reservoir to a gas purge unit (Block B). The dimensions of the two units are given in Fig. 2 and Fig. 3.

Demineralized water is introduced into the system through the outer jacket of the double coil condenser A at the required flow rate, up to a maximum 800 ml/min. Passage through this condenser preheats the sample water being supplied, via a flowmeter to the top boiler. The boiling water from this boiler percolates down the stripping column to the bottom boiler and steam from this boiler passes up the stripping column. The lower boiler supplies sample water to the reservoir via the coils of condenser A and B cooler. The water contained in the reservoir is the supply water for the gas purge unit end is constantly purged with nitrogen gas. This water is transferred to the top of the gas purge column by means of a magnetically coupled pump, operated automatically by a level controller. A counter current of nitrogen or oxygen in nitrogen enters the base of the column through a grade P3 frit, and depending on which gas is being used, oxygen is either removed or added to the sample water. The sample water is drawn from the column through a funnel by means of a magnetically coupled pump, and is supplied to the instrument under test via a sample line which incorporates three 'potter vessels' (Fig. 4), these being used for the chosen reference method, at a flow rate of up to 800 ml/min and a pressure of approximately 0.5 bar.

The maximum sample output from this apparatus can be approximately doubled by using two steam stripping units to supply the sample water reservoir of the gas purge unit.

C-3 OPERATION OF THE RIG

C-3.1 The boiling rate of the water in the bottom boiler must be controlled such that there is a steady flow of steam up the column into the condenser. A high boiling rate will cause flooding in the column and a low boiling rate could cause air to be drawn into the system via the condensers. The correct boiling rate is accomplished by varying the applied voltage to the heating elements and once this applied voltage has been established it need not be varied appreciably when the total water flow is altered. An applied voltage of approximately 150 V is sufficient for the operation of the rig.

C-3.2 The applied voltage required for the heater of the top boiler depends on the temperature of the feed water which in turn, depends on the efficiency of the heat exchanger that is, condenser A. Providing the water contained in this boiler is boiled at a steady continuous rate, the rig will operate satisfactorily, and again, once the applied voltage to the heater has been established, it does not need to be varied appreciably to accommodate changes in sample flow.

C-3.3 The gas flow through the reservoir must be sufficient to prevent air ingress into the vessel when the level pump operates. A buffer volume, that is, several metres of neoprene or nylon tubing are necessary on the outlet of the vessel. The volume of this buffer tube is determined by the quantity of water drawn from the reservoir each time the pump operates and the flow rate of the purge gas. The neoprene tubing also acts as a safety drain in the event of pump failure.

C-3.4 The gas flow rate through the nitrogen purge column is 100 ml to 1 500 ml N_2/min.

C-3.5 The nitrogen purge column must not be allowed to completely fill with water.

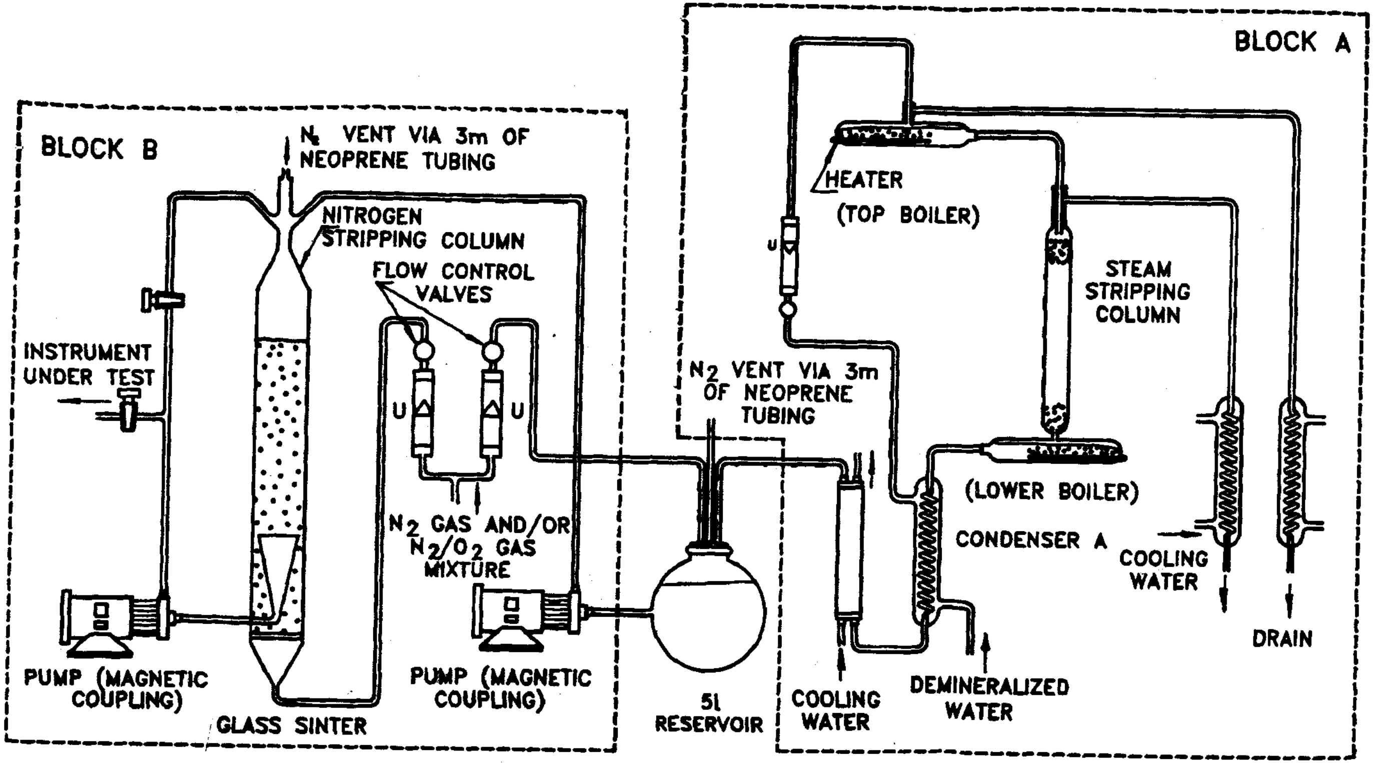


FIG. 1 LABORATORY RIG TO PRODUCE WATER WITH A LOW LEVEL OF DISSOLVED OXYGEN

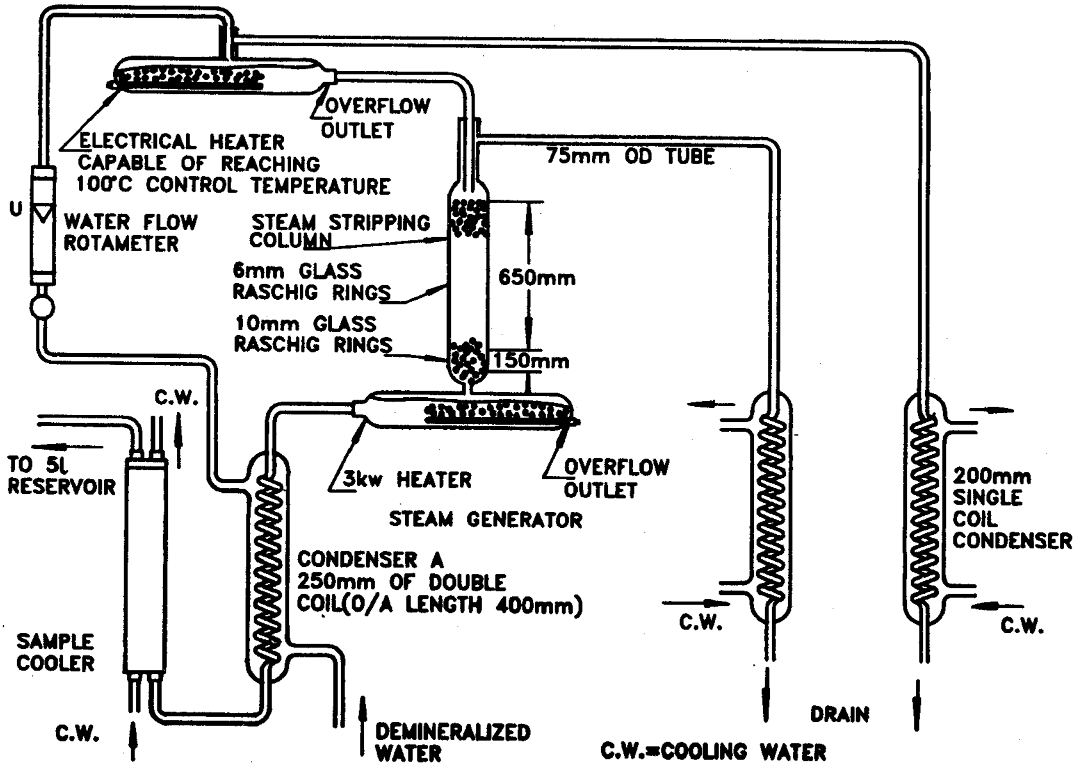
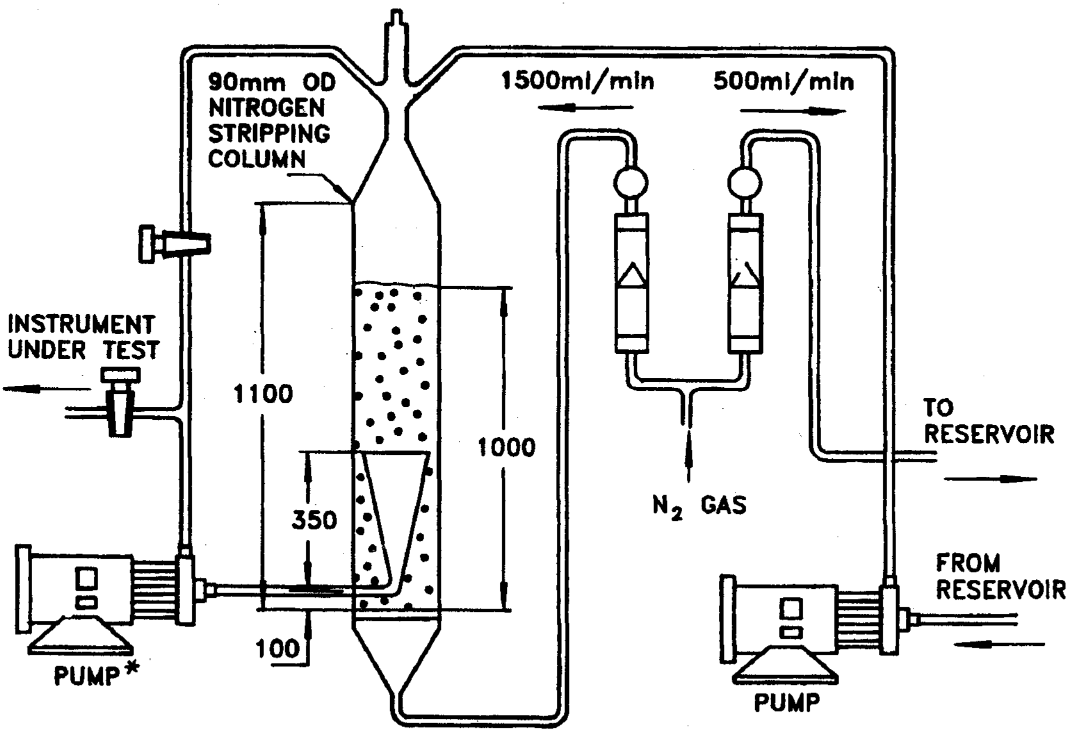


FIG. 2 DIMENSIONS OF BLOCK A



*Pumps are of the magnetically coupled centrifugal type to avoid air in leakage through shaft seals.

All dimensions in millimetres.

FIG. 3 DIMENSIONS OF BLOCK B

C-3.6 (a) *'Stat Up' Procedure*

i) Turn on gas flows, level controller and purge tower feed pump.

ii) Turn on cooling water.

iii) Turn on boiler heaters.

iv) When the water in both boilers is boiling steadily, progressively turn on feed water.

v) When the required water flow rate is established, turn on main offtake pump and balance the input and output flow rates.

vi) Do not allow the gas column to completely fill with water.

(b) *'Shut Down' Procedure*

i) Switch off heaters, feed water and gas.

ii) Allow boilers and coolers to drain.

iii) Switch off level pumps and offtake pump.

iv) Turn off cooling water.

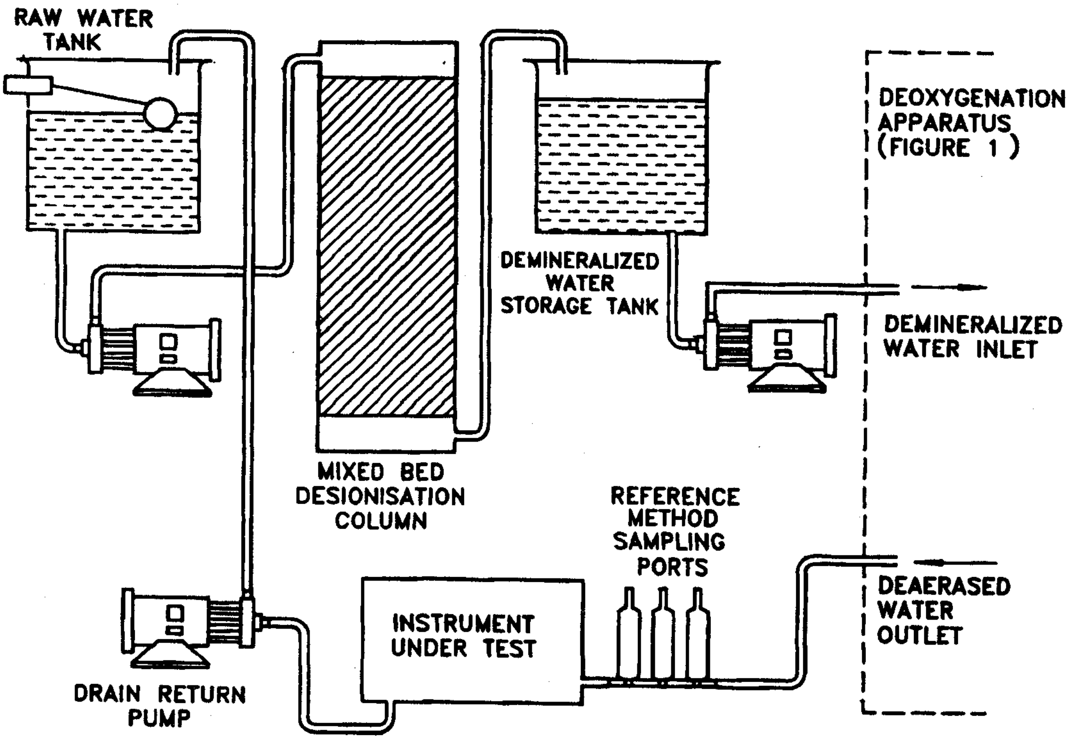

RAW WATER TANK
MIXED BED DESIONISATION COLUMN
DEMINERALIZED WATER STORAGE TANK
DEOXYGENATION APPARATUS (FIGURE 1)
DEMINERALIZED WATER INLET
REFERENCE METHOD SAMPLING PORTS
INSTRUMENT UNDER TEST
DEAERASED WATER OUTLET
DRAIN RETURN PUMP

FIG. 4 COMPLETE SYSTEM FOR LABORATORY TESTING DISSOLVED OXYGEN MONITOR

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